

Radiotracer study of the adsorption of corrosion inhibitors on oxide surfaces modeling the products of metal corrosion.

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In the course of corrosion processes oxidized metal surfaces are formed and the interpretation of overall adsorption phenomena at such interfaces encounters significant difficulties as not easy to distinguish separately the adsorption phenomena occurring on the metal surface and on the layer or submonolayer of oxides and hydroxides formed by corrosion.

This problem should be considered as a question of primordial importance in the case of the investigation and interpretation of the behavior of various, inorganic and organic, corrosion inhibitors.

The possible role of corrosion inhibitors could be summarized as follows:

- The reduction of the dissolution rate of the passivating oxide,
- Repassivation of the surface with repairing or reformation of the oxide film,
- Repair of the oxide film by plugging pores with insoluble compounds
- The prevention of the adsorption of aggressive anions on the surface.

It follows from the considerations outlined above that the interaction of the inhibitors with the corrosion products could play in some cases a central role in the inhibition process. Therefore, the study of this interaction could be a valuable contribution to the clarification of the mechanism of inhibition at least in certain cases.

In accordance with this approach the next crucial problems to be solved are the choice of the appropriate model systems and experimental techniques for the in situ adsorption studies. Hematite and aluminum oxide can be considered as model compounds typical for corrosion products while a widely used example of organic phosphonic acid inhibitor. 1-hidroxy-ethane-1,1-diphosphonic acid (HEDP) and a representative of a new class of environmentally friendly compounds N,N-di-(phosphonomethyl)-glycine (DPG) could be the models for organic inhibitors in addition to the well known inorganic anions as chromate and phosphate.

Radiotracer technique offers a unique possibility of studying sorption phenomena at solid/liquid interfaces in the case of continuous single solid phases and powdered phases as well.

The in-situ methods available for such studies are ranging from techniques applicable to well-defined crystal surfaces to those useful for the study of adsorption phenomena taking place at powdered materials.

As to the role of the labeled species in the radiotracer study of adsorption phenomena, two different versions of the method may be distinguished. The first one, is the direct method. In this case the species to be studied is labeled and the radiation measured gives direct information on the adsorption of this species. However, this method cannot be used in several cases owing to the technical restrictions connected with the very nature of the radiotracer method.

In the case of the so-called indirect radiotracer methods instead of labeling of the species to be studied, another adequately chosen labeled species (indicator species) is added to the system and the adsorption of this component is followed by the usual radiotracer measuring technique.

As the adsorption of labeled sulfate ions at hematite was studied previously in detail ^{35}S labeled sulfate ions were used as ideal indicator species for the investigation at the adsorption of (HEDP) and (DPG) on hematite.

The experimental data obtained confirm the idea that the study of the sorption phenomena-taking place on metal oxides may contribute to the better understanding of

corrosion phenomena.

The indirect radiotracer technique, using labeled sulfate ions as indicator species, proved to be useful to follow the adsorption of inhibitor molecules as the displacement of adsorbed labeled sulfate species (emitting β -radiation) by inhibitors takes place. The relative adsorption strength of various inhibitors (both inorganic and organic ones) can be estimated through their efficiency in the displacement of sulfate ions. It was found that at fixed concentration values the extent of the displacement of adsorbed sulfate species by organic phosphonic acids was higher than that by phosphoric acid and the two phosphono compounds (DPG and HEDP) have different displacement ability (Fig. 1). On the other hand, the effect exerted by phosphoric acid is more pronounced than that found in the presence of CrO_4^{2-} ions.

There is a parallelism between the corrosion inhibitor efficiencies and the adsorbabilities, found through the displacement effect, of the species studied.

Based on this technique, a quick screening method can be developed for the comparison of the affectivity of inhibitor compounds.

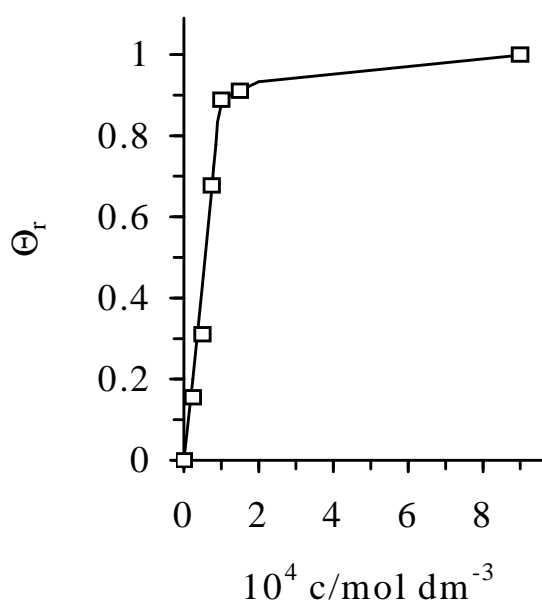


Figure 1. Adsorption isotherm of DPG obtained by indirect radiotracer study using labeled sulfate ions as indicator species